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THERMOCHEMISTRY OF OXYGEN-FLUORINE BONDING

Research Division

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SECOND QUARTERLY TECHNICAL SUMMARY REPORT
CONTRACT NO. NONR 3433(00)

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SECOND QUARTERLY TECHNICAL SUMMARY REPORT
FOR THE PERIOD OF 1 JULY THROUGH 30 SEPTEMBER 1961
Under Contract No. Nonr 3433 (00)

Propulsion Chemistry Branch
Material Sciences Division
Office of Naval Research

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1.0 INTRODUCTION

This report is the Second Quarterly Technical Summary Report issued in partial fulfillment of Contract Nonr 3433 (00). This report covers the work accomplished during the months of July, August, and September.

2.0 TECHNICAL ACTIVITY

2.1 OBJECTIVES OF THE PERIOD REPORTED

The specific objectives of the experimental work performed during this second report period have been the following:

A. Modification of existing experimental equipment for a more detailed study of the synthesis of NO_2F and NO_3F.

B. Further development of consistent and accurate analytical techniques for determination of reaction products in the synthesis of NO_2F and NO_3F. These techniques include mass spectroscopy, gas chromatography, hydrolysis, purification by fractional distillation, and infrared spectrophotometry.

C. Assembly and calibration of a suitable flow calorimeter for measurement of the heats of formation of NO_2F, NO_3F, and ClO_4F.

D. Synthesis and purification of NO_2F from elemental fluorine and nitrogen dioxide and NO_3F from concentrated nitric acid and elemental fluorine.

E. Preliminary evaluation of the heat of formation of NO_2F from measurement of the heat evolved during reaction of elemental fluorine and nitrogen dioxide.

2.2 STUDY OF NO_2F

2.2.1 Synthesis

The reaction involved in synthesizing NO_2F from F_2 and NO_2 appears

not to be as clear cut as heretofore believed. To date, the concentration of the by-products in the reaction $1/2F_2 + NO_2 = NO_2F$ is not known with sufficient precision and accuracy to define an absolute value of the heat of formation of NO_2F from the calorimetric studies.

2. 2. 2 Analyses

A. The mass spectrometric studies show an abnormally large percentage of hydrogen fluoride in purified samples of NO_2F prepared via the NO_2 and F_2 reaction.

The source of HF has not been completely established. The introduction of NO_2F into the mass spectrometer may produce HF since introduction of F_2 into the mass spectrometer system generates excessive amounts of HF. This might be expected also with NO_2F since NO_2F is essentially as reactive as F_2. On the other hand, NO_2F appears to be stable at extremely low pressures in the mass spectrometer.

B. An infrared spectrum of the synthesized and purified NO_2F is shown in Figure 1. The spectrum agrees well with the published spectra of NO_2F.* The peaks at 822, 1312, and 1793 cm^{-1} are characteristic of NO_2F.

C. The hydrolysis system fabricated of glass and the coating of inert wax were found to give insufficiently precise results for analysis of NO_2F. A reaction of NO_2F with the glass and wax system gives spurious results. To circumvent many of the inherent problems of using glass and wax with fluorine-containing

* Dodd, R.E., J.A. Rolfe, and L.A. Woodward, "Infrared and Raman Spectra of Nitryl Fluoride, "Trans. Faraday Soc., 52, 1956.

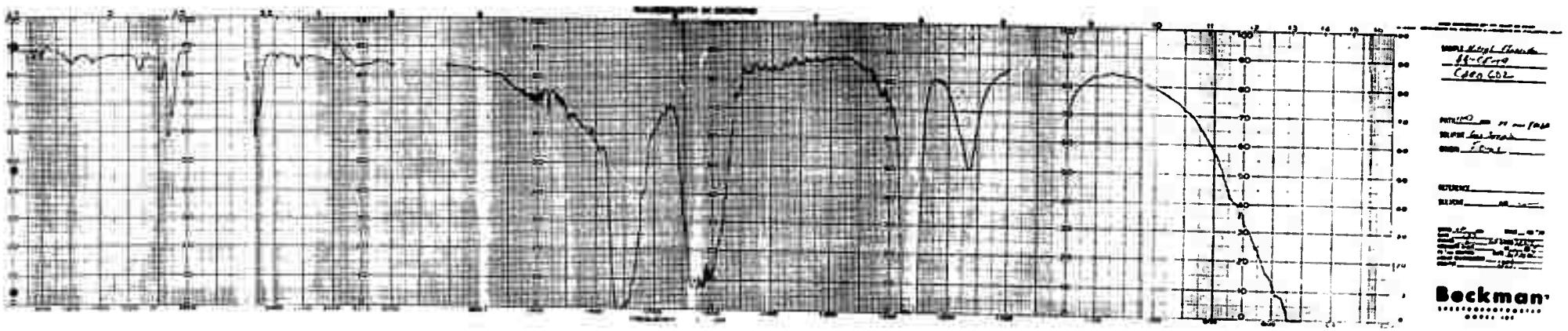

FIGURE 1. INFRARED SPECTRUM OF NITRYL FLUORIDE (NO_2F)

materials, a special hydrolysis system fabricated completely of Kel-F has been assembled. This system is ready for operation.

Monel and other metals cannot be used in the fabrication of fluoride hydrolysis systems since the hydrolyzing medium readily dissolves the protective metal-fluoride coatings. The dissolved metal fluorides in turn interfere with the hydrolysis reaction. The use of Kel-F or Teflon for fabrication circumvents this problem.

The hydrolysis analyses obtained in the original glass and wax system are insufficiently precise for reporting at this time.

D. The gas chromatography results are inconclusive. The retention volumes of F_2, NO_2F, and HF are essentially the same on a 25 foot column packed with Kel-F oil and Kel-F powder. Thus, a reasonable resolution of characteristic peaks for a mixture of F_2, NO_2F, and HF has not been possible with chromatographic analysis. Attempts will be made to evaluate other packing materials in the chromatography column.

2.2.3 Heat of Formation - Calorimetry

As discussed in the preceding quarterly report, the heat of formation of NO_2F will be measured directly from its synthesis by the NO_2 - F_2 reaction in a flow calorimeter. Figure 2 is a photograph of the assembled calorimetric system and support equipment. The calorimeter is complete and has been calibrated for heat capacity. The heat capacity of the system is 1.585 kcal/^{o}C.

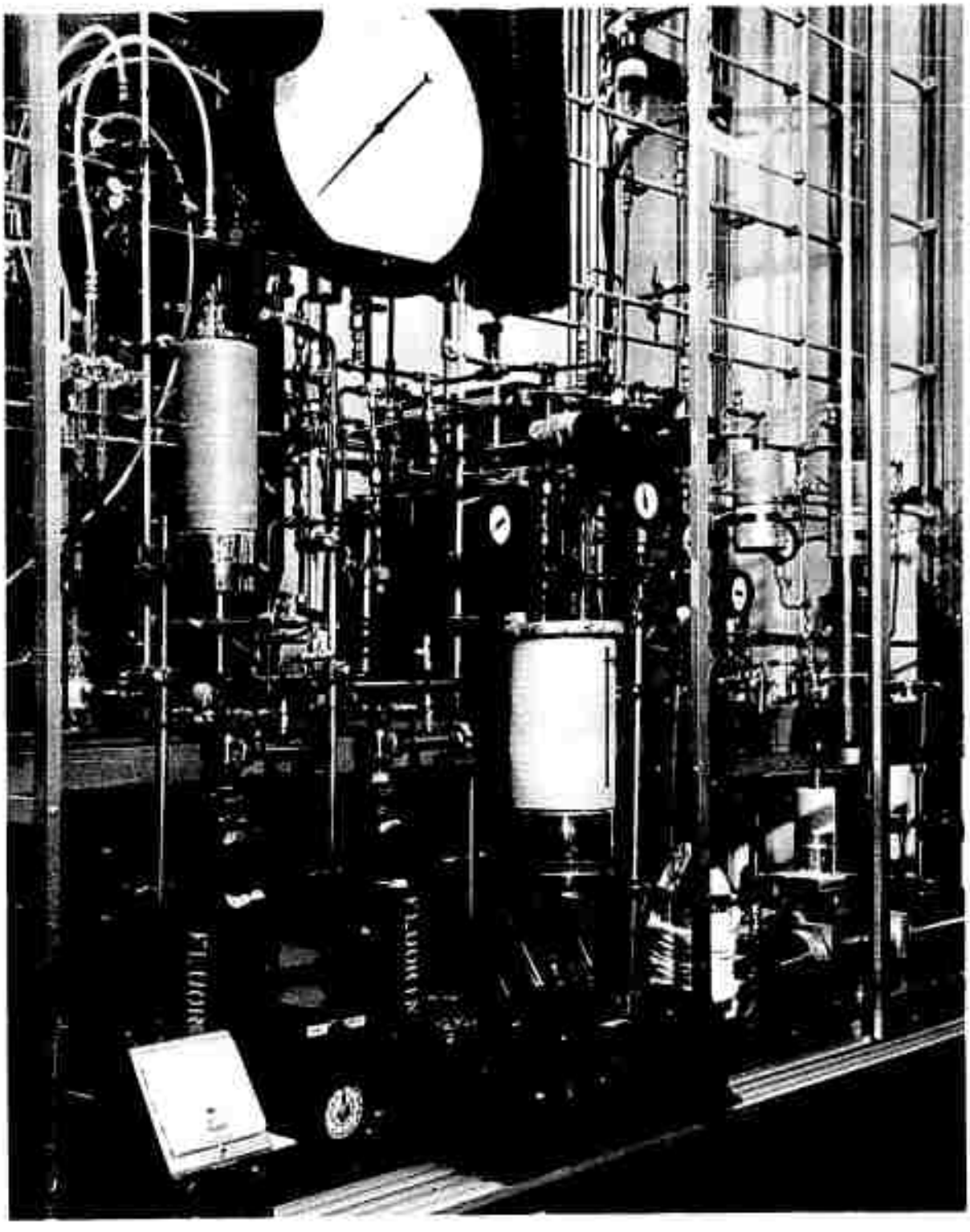

FIGURE 2. ASSEMBLED CALORIMETRIC SYSTEM AND SUPPORT EQUIPMENT

Several checkout experiments have been completed on the heat of formation of NO_2F, using the flow calorimeter shown in Figure 2. A typical time-temperature curve for a NO_2F heat of formation determination is shown in Figure 3. The important data for this run are listed in Table I. The heat of formation is derived from the measurements utilizing Hess's law.

The heat of formation per mole of NO_2F utilizing the reaction

$$1/2\ F_2 + NO_2 \longrightarrow NO_2F \qquad (1)$$

and Hess's law is:

$$\Delta H_f(NO_2F) = \Delta H_f(1/2\ F_2) + \Delta H_f(NO_2) + \Delta H_r \qquad (2)$$

The standard heat of formation of NO_2 is accurately known and has a reported value of 8.091 kcal/gmol* while the heat of formation of F_2 is zero by definition. With the insertion of the appropriate values of the terms in Equation 2, the heat of formation per mole of NO_2F becomes

$$\Delta H_f(NO_2F) = 8.091 + \Delta H_r$$

* Rossini, et. al., Circular of the National Bureau of Standards, 500, U.S. Government Printing Office, Wash., D.C., 1952

TABLE I. EXPERIMENTAL DATA OF CHECKOUT RUN FOR HEAT OF FORMATION OF NO_2F

Moles NO_2 used	= 0.060
Moles NO_2F formed	= 0.052
Percent yield	= 87%
Heat Capacity of Calorimeter	= 1.585 kcal/°C
Temperature rise of Calorimeter	= 0.910°C

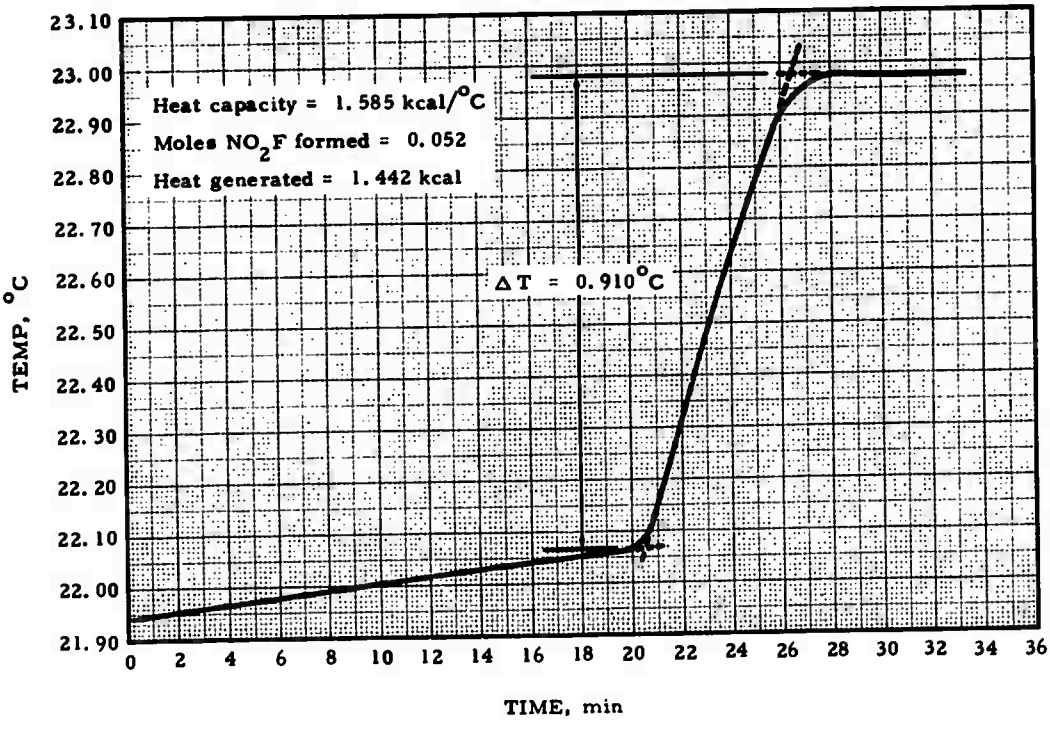

FIGURE 3. TEMPERATURE VERSUS TIME CURVE IN CALORIMETER FOR NO_2F FORMATION REACTION

A preliminary heat of formation of NO_2F as determined from this experiment is -20 ± 5 kcal/gmol. The heat of formation of NO_2F derived from these checkout studies is not sufficiently accurate for final reporting because the analysis of NO_2F is insufficiently prccise and accurate at this time to establish the concentrations of the primary and secondary reaction products. The purity of the NO_2F for the experiment listed in Table I was determined by a simple fractionation only.

2.3 STUDY OF NO_3F

2.3.1 Synthesis

NO_3F has been synthesized in low yields directly from concentrated HNO_3 and F_2. The yield in the present synthesis equipment is in the order of 10 percent based on the amount of fluorine used (HNO_3 is in excess). Modifications of the reactor for a longer contact time are necessary for larger conversions.

2.3.2 Analysis

A. The NO_3F is being analyzed initially by hydrolysis. A typical synthesis product of NO_3F after purification by distillation gives the following results upon hydrolysis. These results are listed in Table II.

NO_3F hydrolyzes according to the reaction

$$NO_3F + H_2O \longrightarrow HNO_3 + HF + \tfrac{1}{2}O_2$$

The reaction should give equal moles of NO_3^- and F- and twice the moles of H^+ upon hydrolysis. The results in Table II are essentially correct for NO_3F. The size of the sample of NO_3F hydrolyzed as reported in Table II was 7.6 millimoles indicating a purity of approximately 70 percent NO_3F.

TABLE II. HYDROLYSIS RESULTS OF PURIFIED NO_3F

NO_3^-	5.27 millimoles
F-	5.10 millimoles
H^+	10.69 millimoles

B. The infrared spectra of the NO_3F synthesized is shown in Figure 4. This agrees well with the spectra reported.* The prominent absorption bands at 920, 1030, 1430, 1950, and 3060 cm^{-1} are characteristic of NO_3F.

2.4 STUDY OF ClO_4F

The synthesis, purification, and analysis of ClO_4F will begin as soon as satisfactory results on NO_2F and NO_3F are obtained.

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* W. E. Skiens and G. H. Cady, "Thermal Decomposition of Fluorine Nitrate," J. Am. Chem. Soc. 80, 5640 (1958).

FIGURE 4. INFRARED SPECTRA OF FLUORINE NITRATE (NO_3F)

3.0 FUTURE WORK

Synthesis, analysis, and purification of NO_2F will be continued to provide more quantitative information on the $NO_2 + F_2$ reaction. The calorimetric studies will be completed upon satisfactory resolution of the reaction products.

Synthesis, analysis, and purification of NO_3F will be continued to provide more quantitative information on the F_2 + (conc) HNO_3 reaction. Conversions greater than the present 10 percent are required to permit accurate measurement of the heat of formation of NO_3F. Continued effort will be expended to obtain greater conversions. The calorimetric studies will be initiated upon satisfactory resolution of the reaction products.

The O-F bonded compound ClO_4F will be synthesized and the composition of the reaction products will be established.

Vapor pressures and densities will be measured for NO_2F, NO_3F, and ClO_4F.

There will be a theoretical correlation of these data to obtain reliable information on the stability and properties of O-F bonded compounds.

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